doi:10.1017/S1431927622007383

Microsc. Microanal. 28 (Suppl 1), 2022

Rhodium Doping of Strontium Titanate for Enhanced Visible Light Absorption

Piyush Haluai[1]* and Peter A. Crozier[1]

[1.] School for Engineering of Matter, Transport & Energy, Arizona State University, Tempe, Arizona, United States.
*Corresponding author: phaluai@asu.edu

Ever since the discovery of electrochemical photolysis of water using anatase [1], a lot of attraction has been focused on the development of materials that can harvest the energy from photons and generate solar fuels. For example, photocatalytic water splitting using semiconductor-based materials is one way of harvesting solar energy to generate H_2. Absorbed the solar energy (photons) is converted to electron-hole pairs which act as charge carriers and reduce and oxidize the water respectively [2]. Most used materials with high structural stability under the reaction are oxides but they suffer from poor efficiency due to their bandgaps being in UV part of the spectrum which constitutes 3-4% of the solar spectrum [3]. Tuning the bandgap by doping has gained a lot of interest and proven to be quite successful in making these oxides that absorb in the visible part of the spectrum. In this work, we aim to investigate the effects of rhodium (Rh) doping in strontium titanate (STO) and associated visible light absorption properties. We have chosen a model photocatalyst consisting of Ni/NiO core-shell co-catalyst loaded on a Rh doped STO, since this type of core-shell structure loaded on semiconductor has previously shown overall water splitting [4].

Multifaceted Rh doped STO nanoparticles were synthesized using a solid state reaction method followed by ball milling as reported by [5]. X-ray diffraction (XRD) measurements showed peaks attributable to STO only, indicating phase purity. A 5 wt.% loading of Ni/NiO co-catalyst was deposited onto the Rh doped STO using dry impregnation and thermal processing methods as described by Zhang et al. in [4]. As-synthesized and Rh doped STO were imaged using transmission electron microscopy (TEM) in an aberration-corrected FEI Titan TEM operated at 300 kV and equipped with a Gatan K3 direct electron detector for imaging. Photocatalytic water splitting over the Ni/NiO-loaded Rh doped STO was performed with a liquid-phase photoreactor coupled to a gas chromatograph for compositional analysis of H_2. A Xe arc lamp operated at 350 W was used as a light source. Methanol was used as hole scavenger; hence no oxygen was detected.

Figure 1 displays TEM images of the as-synthesized Rh doped STO nanoparticles, which are roughly 100 – 200 nm in size (figure 1a). Strain contrast arising from the defects present in the nanoparticles due to the doping of Rh (figure 1b). The high- resolution TEM images reveal clean nanoparticle surfaces and no overhanging Rh nanoparticles suggesting all the Rh has gone in the STO lattice. **Figure 2** plots the UV-Vis diffuse reflectance spectroscopy data showing the optical properties of the material. It can be seen that upon Rh doping there's a peak appearing at ~580 nm corresponding to Rh^{4+} [5]. Corresponding bandgap values calculated form the UV-Vis spectra also shows a redshift of the bandgap onset upon Rh doping into STO (changes from 3.2eV of pure STO to 2.11-2.75eV in Rh doped STO). Photocatalytic water splitting under visible light with the Ni/NiO co-catalyst showed H_2 evolution suggesting a successful doping of STO with Rh to tune the catalyst for visible light absorption. We are currently studying the effect of the Rh oxidation state. (+3 or +4) on H_2 generation from water under visible light illumination. Electron energy loss spectroscopy (EELS) mapping in scanning transmission mode (STEM) is currently being used to determine the location of Rh atoms in the lattice sites. *In situ* electron microscopy coupled with visible light illumination using the Thermo-Scientific Titan AC-ETEM microscope is also being used to investigate the effect of charge transport across the semiconductor and co-catalyst interface [6].

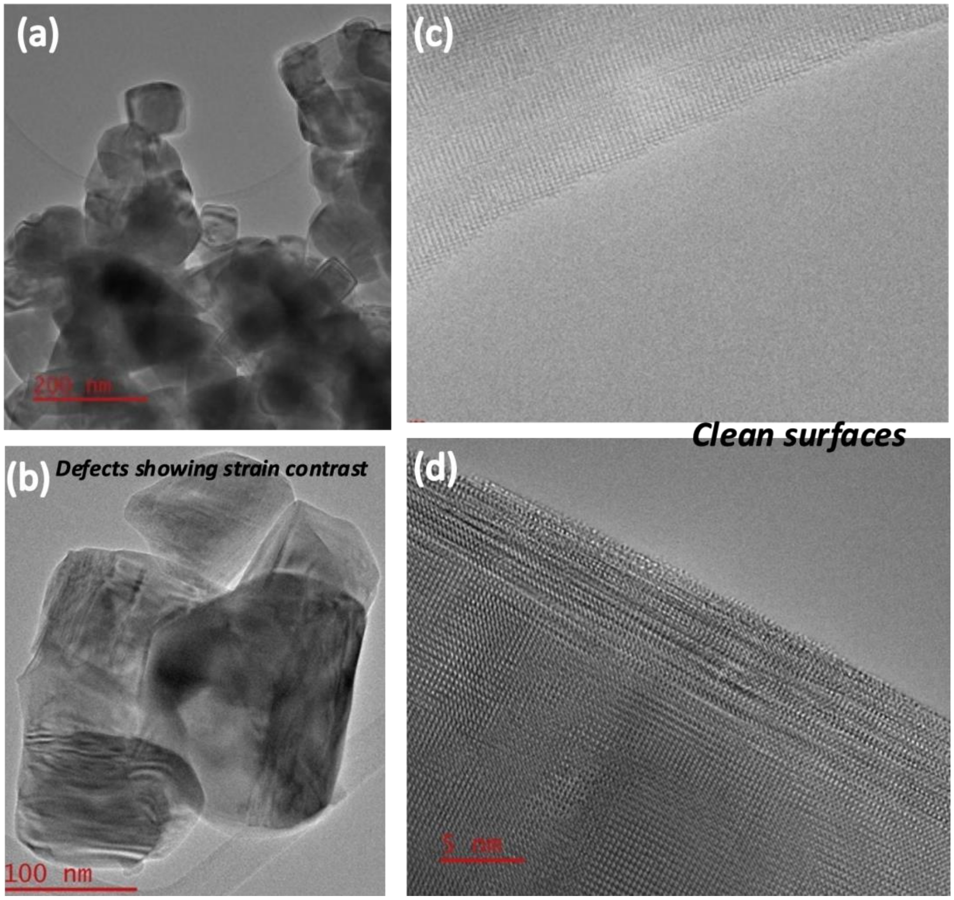
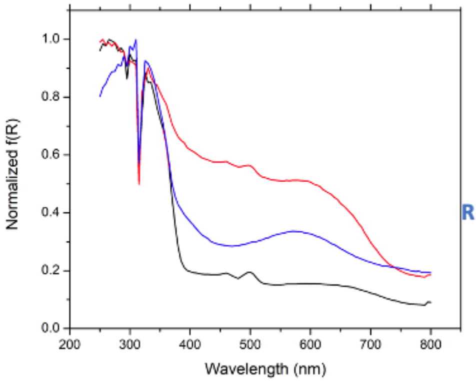


Figure 1. (a) and (b) shows low magnification TEM images showing nanoparticles of Rh doped STO in the size range of 100-200nm. (c) and (d) shows cleaner nanoparticle surfaces after. In (b) strain contrast arising from possible defect incorporation during doping is visible.



Sample	Bandgap (nm)	Bandgap (eV)
STO Cubes	404	3.06
Rh doped STO_SSR	588	2.11
Rh doped STO_SSR_Post Ball Milling	451	2.75

Figure 2. Graph showing the UV-Vis diffuse reflectance spectra from different materials. Spurious peaks at ~450nm and ~500nm are visible and possibly arising from detector artifact. Rh doped STO clearly shows the presence of an extra peak at ~580nm. The table next to the graph shows the bandgap values measured from the spectra using Kubelka-Munk method. The colors are matched in the graph and the table.

References:

[1] A Fujishima and K Honda, Nature **238** (1972), pp. 37. doi: 10.1038/238037a0
[2] T Hisatomi, J Kubota and K Domen, Chem. Soc. Rev. **43** (2014), p. 7520. 2014, doi: 10.1039/C3CS60378D
[3] DHK Murthy et al., Sustain. Energy Fuels **3** (2019), p. 208. doi: 10.1039/C8SE00487K
[4] Q Liu, L Zhang and PA Crozier, Appl. Catal. B Environ. **172** (2015), p. 58. doi: 10.1016/j.apcatb.2015.01.008
[5] Y Yamaguchi et al. Chem. Lett. **45** (2016), p. 42. doi: 10.1246/cl.150907

[6] We gratefully acknowledge support of DOE grant BES DE-SC0004954, the use of ASU’s John M. Cowley Center for High Resolution Electron Microscopy.